1972

Economic study of design condition for a H2-CO plant

Phil K. Roth
Lehigh University

ECONOMIC STUDY OF DESIGN CONDITIONS FOR A H_2-CO PLANT

A PROJECT REPORT BY

PHIL K. ROTH
CHEMICAL ENGINEERING DEPARTMENT
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA
JANUARY 10, 1972

ACKNOWLEDGEMENT

I would like to thank Arthur D. Bixler for his supervision and assistance on this project. Thanks also goes to other members of the Air Products and Chemicals group who offered their assistance and to Miss Claire Hieter and Dianne Roth who helped prepare the final draft for this report. Dr. L. A. Wenzel receives my appreciation for his guidance throughout this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Design conditions for the LaPorte II H_2-CO plant, owned by Air Products and Chemicals Incorporated, were investigated in order to relate them to plant economics. This study was centered around the operating conditions of the reformer. Forty two combinations of reformer temperatures and pressures were studied. Outlet temperatures ranged from 1550 ^{o}F to 1800 ^{o}F. Outlet pressures ranged from 100 psia to 250 psia. For each case costs for major equipment items affected by reformer operating conditions were determined as well as related operating costs. These costs were converted to annual investment charges. The economic data for each case was then compared to the current LaPorte II case which has a reformer designed to operate at an outlet condition of 1650 ^{o}F and 185 psia. The results of this study indicated that the LaPorte II case could have been improved economically if the reformer had been designed to operate at 1750 ^{o}F and 175 psia. The annual investment for these reformer operating conditions would have been 2.1% less than for the original LaPorte II design conditions.

INTRODUCTION

Air Products hydrogen-carbon monoxide facility, located in and serving the LaPorte, Texas area, is currently in the expansion stage. An additional facility, hereafter referred to as LaPorte II, is now under construction and scheduled for start-up in April of 1972. LaPorte II is designed for a maximum production rate of twelve million standard cubic feet per day of hydrogen product and four million standard cubic feet per day of carbon monoxide product. Together with the existing LaPorte I plant it is expected that the expanded facility will be capable of meeting short term market demands for hydrogen and carbon monoxide as set by more than five customers located in and around the LaPorte area.

The LaPorte II plant operating conditions were established during the design stage of the plant. However, Air Products felt the need for investigating these conditions to see whether more economical conditions exist, in the event similar facilities would be built. This project conducts such a study.

The objective of this project, then, is to investigate variations on the original LaPorte II operating conditions and relate them to plant economics. The process flowsheet of the LaPorte II plant will not be altered but both operating and design conditions are allowed to change. The final hydrogen and carbon monoxide product rates will remain constant

for all variations on operating conditions. These rates will be the same as designed for in the original LaPorte II plant. Variations on operating conditions will be centered around the reformer. Costs for major equipment items as well as related operating costs affected by changes in reformer operating conditions will be determined. This information will then be converted to an annual investment charge which will be compared to the original LaPorte II annual investment charge. Cost information will be supplied from the original LaPorte II budget study.

PLANT PROCESS DISCUSSION

A brief description of the LaPorte II process will aid in understanding the affects of various operating parameters on the plant economics. Refer to Figure 1 for the following process description.

The plant can be divided into two main sections. The first of these is the reforming section. Here natural gas, steam, carbon dioxide recycle from the carbon dioxide separation system and a carbon monoxide-methane recycle stream are preheated to 900 ^{o}F and fed to a reformer at an inlet pressure of about 235 psia. In the reformer the following primary reactions occur:

$$(1) \qquad CH_4 + H_2O \xrightarrow{K_r} CO + 3H_2$$

$$(2) \qquad CO + H_2O \xrightarrow{K_s} CO_2 + H_2$$

The first reaction is called the reforming reaction. The equilibrium constant, K_r, increases with increasing temperature (see Table 3). Decreasing pressure favors the production of carbon monoxide and hydrogen for this reaction. The second reaction is called the water-gas shift reaction. The equilibrium constant, K_s, increases with decreasing temperature. Pressure has little affect on the carbon dioxide production for this reaction. The LaPorte II reformer is designed to

operate at an outlet temperature of 1650 °F and 185 psia. Combustion of natural gas in the reformer supplies the heat necessary to raise the process stream temperature to 1650 °F and, at the same time, supplies the heat of reaction.

The reformer effluent process stream consists of hydrogen, carbon monoxide, carbon dioxide, methane, inerts (nitrogen present in the natural gas feed) plus steam. The heat content of this high temperature stream is recovered in a series of quenching and cooling steps and put to use in other plant processes. As the temperature of the process stream drops, water begins to condense out under its own partial pressure. At 100 °F only a small fraction of water is still present in the process stream.

The major portion of carbon dioxide in the process stream is removed by MEA absorption. The carbon dioxide is then stripped from the rich MEA solution, compressed and made available as recycle to the reformer feed. After the major portion of water and carbon dioxide are removed, the process stream is compressed to about 310 psia and then sent through molecular sieve driers to reduce the carbon dioxide and water concentrations to a low PPM range. This stream is now sent on to the second main section of the plant, the separation section.

The process stream, at 45 °F and 300 psia, enters the cold box. At this point the stream consists only of carbon monoxide, hydrogen,

methane and nitrogen. The carbon dioxide and water were removed from the process stream prior to entering the cold box to avoid freeze-out and clogging in the cold box exchangers. As the stream is cooled, partial condensation occurs whereby a large portion of the carbon monoxide and methane are separated from the hydrogen. As the temperature drops to -335 °F all but a fraction of the hydrogen is removed from the main process stream. This hydrogen stream then leaves the cold box as an impure hydrogen product. The liquid stream near -335 °F and 280 psia is now largely carbon monoxide and methane with only a few percent hydrogen. The hydrogen in this liquid stream is stripped out and the resulting carbon monoxide and methane stream is distilled. The overhead gas from the distillation column leaves the cold box and becomes the final carbon monoxide product. The bottoms from the column consists of a 50-50 mixture of carbon monoxide and methane which, after leaving the cold box, is compressed and recycled to the reformer as feed.

Refrigeration requirements of the cold box are supplied from two sources. The first source is the high pressure process stream entering the cold box. A fraction of the refrigeration is supplied through pressure letdown of the various process streams in the cold box from 300 psia to 15 psia (the hydrogen product stream from the cold box is the only portion of the original process stream which is not letdown in pressure). However, the larger portion of the cold box refrigeration is supplied by a closed nitrogen loop. Here nitrogen is compressed to

about 73 psia and cooled to 100 °F before entering the cold box. In the cold box a portion of this nitrogen stream is turbo-expanded to 15 psia, cooling to -311 °F. This low temperature stream is used to cool the incoming process stream. The remaining high pressure nitrogen stream is letdown in pressure through a valve to 15 psia, providing more refrigeration. A portion of this stream experiences another pressure letdown to about 4 psia to supply the low temperature requirement of -336 °F for partial condensation of the process stream. The low pressure and intermediate pressure nitrogen streams coming from the cold box are then recompressed to the high pressure of 73 psia, cooled to 100 °F and fed back to the cold box.

Before delivery to customer stations the carbon monoxide product coming from the cold box is compressed from 15 psia to about 210 psia. Table 1 shows the final carbon monoxide product specifications and flow rates for the LaPorte II plant.

The hydrogen product from the cold box contains about two percent carbon monoxide which must be removed in order to meet customer requirements. To perform this carbon monoxide removal the hydrogen product stream is sent to a low temperature shift converter (LTS) where the following reaction occurs:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

This reaction is the same as the water-gas shift reaction which occurs in the reformer. As previously mentioned, it is favored at low temperature. As a result, the low temperature shift converter is operated at about 425 ^{o}F, considerably lower than the reformer temperature.

The carbon dioxide present in the low temperature shift converter effluent is removed by MEA absorption and then stripped from the rich MEA solution for recycle to the reformer. Trace quantities of carbon monoxide and carbon dioxide still remain in the hydrogen product and are removed by methanation. The methanation reactions are as follows:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

The methanator effluent stream is now the final hydrogen product. The small quantity of methane in this stream can be tolerated. Since the hydrogen product leaves the cold box at a pressure of about 260 psia it is not necessary to compress the final hydrogen product before delivery to the customer station. Table 1 shows the final hydrogen product specifications and flow rates for the LaPorte II plant.

The plant steam system provides high pressure steam and liquid for quenching the process stream after leaving the reformer. It also provides auxiliary reboiler heat for the MEA stripping column and

reactivation heat for the natural gas desulfurizers. A number of pumps are steam driven as well as the large nitrogen compressor which supplies cold box refrigeration. This steam is generated by recovering available waste heat of which the largest portion is supplied by the reformer flue gas. Cooling the flue gas from about 1800 ^{o}F to 400 ^{o}F generates about 38,000 pounds of steam per hour at about 630 psia and 725 ^{o}F. The remainder of heat supplied to the steam system comes from the cooling of the high temperature process stream leaving the reformer.

PROJECT CRITERION

Before work was started on this project certain guidelines were established. This section discusses those guidelines in an effort to clarify the scope and nature of the work involved in the project.

It was decided that the LaPorte II plant was to serve as the reference case. This choice was made for several reasons. The economic data relating to this plant is current information. As a result, this data should yield good results when the economics of various operating conditions are investigated. General and specific information on this plant was also more readily available since the entire process design for the LaPorte II project was done by Air Products personnel.

Since Air Products has a good understanding of cryogenic systems it was felt that little could be done to significantly improve cold box operating conditions. Thus, it appeared that changes ir operating conditions in the reformer should receive the main attention. As a result, emphasis was placed on investigating the LaPorte II reformer. The final hydrogen and carbon monoxide product rates, as well as compositions of these streams, were to remain the same, regardless of any changes in operating conditions. This meant that the cold box and equipment following the cold box remained the same in size and cost for all cases studied. The assumption here was that the compositions of all

streams leaving the cold box would remain the same as the original LaPorte II conditions regardless of changes in reformer operating conditions.

The reformer performance was controlled by three primary conditions. These were (1) the operating temperature (2) the operating pressure and (3) the methane leakage through the reformer. Combinations of these three conditions were studied to determing their affect on equipment as far as economics was concerned. The reformer inlet temperature was always held constant at 900 ^{o}F while the outlet temperature was varied from 1550 ^{o}F to 1800 ^{o}F at 50 ^{o}F intervals. The outlet pressures ranged from 100 psia to 250 psia at 25 psia intervals. The inlet pressure was set by the outlet pressure plus the pressure drop through the catalyst filled reforming tubes. This pressure drop averaged about 40 psia.

The term methane leakage is defined as the amount of methane which "leaks" through the reformer unreacted. For this project the methane leakage was referred to as the fraction of methane present in the reformer effluent on a carbon dioxide and water free basis. This methane leakage was stringently controlled in order to avoid carbon formation in the catalyst filled tubes. The formation of carbon would cause catalyst poisoning, a condition which is highly undesirable. As a result, a criterion was established which allowed the selection of the appropriate methane leakage for each case of reformer temperature

and pressure. The calculation procedure for selecting methane leakage is presented in the following paragraphs.

The concept of an "approach to equilibrium" was used in calculating the reformer effluent and feed conditions (illustrated in the calculation section). Back calculation from the final carbon monoxide and hydrogen products yielded the following reformer effluents after a value for the methane leakage had been assumed: methane, carbon monoxide, hydrogen and nitrogen. The only unknowns were the effluent carbon dioxide and water. The simultaneous solution of the following two primary equations, related to the reactions in the reformer, yielded the carbon dioxide and water effluents:

$$(1) \quad CH + H_2O \xrightarrow{K_r} CO + 3H_2 \; : \qquad K_r = \frac{(P_{CO})\,(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$$

$$(2) \quad CO + H_2O \xrightarrow{K_s} CO_2 + H_2 \; : \qquad K_s = \frac{(P_{CO_2})\,(P_{H_2})}{(P_{CO})\,(P_{H_2O})}$$

where P_i equals the partial pressure of component i. The question arose as to what value should be selected for the two reaction constants, K_r and K_s, used in the above mentioned equations. Since the water-gas reaction is rapid it was assumed that this reaction reached equilibrium at the reformer outlet temperature. Thus, K_s was determined from the

outlet temperature (see Table 2 for K_s versus temperature). The reforming reaction is somewhat slower. As a result, it was assumed that, at the outlet, this reaction reached the equilibrium value of a slightly lower temperature than the outlet temperature. The difference between this lower temperature and outlet temperature is called the "approach to equilibrium". Since the reaction rate (not related to K_r) increases with increasing temperature, a smaller "approach to equilibrium" was selected as the temperature increased (see Table 4 for the relationship between the reformer outlet temperature and the "approach to equilibrium"). This concept of an "approach to equilibrium" is used by reformer catalyst vendors, having been developed from past reformer operating experience. The "approach to equilibrium" for a specified outlet temperature is governed by a number of conditions such as catalyst effectiveness, flow rate of the gas and residence time of the gas in the reformer tubes. The "approach to equilibrium" values listed in Table 4 correspond to the type of reformer operating conditions which were studied.

From the known reformer effluent composition the feed composition was calculated using material balances. With the known feed composition a series of theoretical intermediate and an outlet composition were calculated. These theoretical calculations assumed that the two reformer reactions were always at equilibrium. From these theoretical calculations the following carbon formation constants were calculated:

(1) $CH_4 \xrightarrow{K_1} 2H_2 + C$: $\qquad K_1 = \dfrac{(P_{H_2})^2}{(P_{CH_4})}$

(2) $H_2O + C \xrightarrow{K_2} H_2 + CO$: $\quad K_2 = \dfrac{(P_{H_2})(P_{CO})}{(P_{H_2O})}$

(3) $2CO \xrightarrow{K_3} CO_2 + C$: $\quad K_3 = \dfrac{(P_{CO_2})}{(P_{CO})^2}$

These three reactions are the primary carbon formation reactions. The methane leakage used in calculating the actual reformer effluent had to be selected (for each case of outlet temperature and pressure) such that the theoretical carbon formation constants fell on the acceptable operating curves of Figures 2, 3 and 4. This meant that only one best value for methane leakage could satisfy the carbon formation criterion for each set of temperature and pressure.

The basis of the carbon formation curves (Figures 2, 3 and 4) stemmed from the economic consideration of the size of the carbon dioxide removal system. The lower the methane leakage in the reformer, the greater the quantity of carbon dioxide in the effluent. The greater the quantity of carbon dioxide, the larger and more costly the carbon dioxide removal system. However, the higher the methane leakage, the greater the possibility of carbon formation in the reformer. The acceptable operating curves on Figures 2, 3 and 4 (developed from information supplied by reformer catalyst vendors) represent the operating conditions which allow the maximum methane leakage without undue risk of carbon formation.

The affect of methane leakage on cold box refrigeration requirements was also studied. This aspect was considered since refrigeration requirements dictate the size and cost of the nitrogen compressor.

The final criterion was that the carbon monoxide-methane recycle stream from the cold box to the reformer was set at a 50-50 mixture for all reformer operating conditions.

In summary, the following guidelines were established:

(1) The LaPorte II plant served as the base case, using the same process design and maintaining the same hydrogen and carbon monoxide production rates.

(2) Reformer operating conditions were studied in an effort to determine their affect on economics (cold box operating conditions remained the same for all cases of reformer operating conditions studied).

(3) Temperature, pressure and methane leakage were the three primary variables for controlling the operation of the reformer.

(4) The "approach to equilibrium" concept was used in calculating reformer effluent, feed and theoretical conditions.

(5) Figures 2, 3 and 4 served as the carbon formation criterion.

(6) Cold box refrigeration requirements were investigated and related to the size and cost of the nitrogen compressor.

(7) The carbon monoxide-methane recycle stream from the cold box to the reformer feed was set at a 50-50 mixture for all cases studied.

ECONOMIC EVALUATION

Reformer operating conditions were investigated for a total of 42 different cases. These operating conditions ranged in temperature from 1550 ^{o}F to 1800 ^{o}F and ranged in pressure from 100 psia to 250 psia. For each case the cost of the following major process equipment was determined:

(1) the reformer (including auxiliary equipment)

(2) the carbon dioxide removal system (including the carbon dioxide-MEA separation system)

(3) the following compressors:

   a. cold box compressor

   b. carbon monoxide-methane recycle compressor

   c. carbon dioxide recycle compressor

   d. carbon monoxide compressor

(4) the nitrogen refrigeration compressor

The following operating costs were also determined for each case:

(1) the reformer fuel consumption

(2) the electrical power consumption used to drive the compressors in (3) plus small electrical equipment in the carbon dioxide removal system

The above mentioned equipment items were considered because they represented those items most affected by reformer operating conditions. They also represented the larger and more costly items of the plant.

The cold box, although it was also a costly item, was not included in this group of equipment because, as mentioned previously, it was assumed that operating conditions in it were not affected by reformer operating conditions. As a result, its design and size were unchanged for all 42 cases studied.

Although the size and cost of the carbon monoxide product compressor remained unchanged for each case studied, it was included in the above equipment for the following reason: The four compressors listed in (3) physically exist as one unit which is referred to as a multiservice compressor. In order to determine a cost of this compressor for each case, the total brake horsepower (BHP) had to be known. Thus the constant BHP of the carbon monoxide product compressor had to be added into the total BHP for each case.

The remaining equipment, such as heat exchangers, quench pots, condensate traps and driers were not considered in the economic picture for each case even though the size and cost of such equipment may have changed from case to case. It was felt that the cost of such equipment would not significantly alter the final plant cost for each case since these items (excluding the cold box) represented only a small fraction of the total equipment cost for the LaPorte II plant.

For each case studied the cost of the equipment considered was determined. This cost was converted to an annual equipment investment

charge by multiplying by the factor .323. This factor includes allowances for maintenance, depreciation, insurance, taxes, general and administrative charges (G&A), and gross profits on an annual basis. To this annual equipment investment charge was added the operating costs of reformer fuel and electrical power. This total represented the annual investment charge only for those items considered (not the total plant annual investment charge). The relative differences of these annual investment charges for the cases studied were used to determine the most economical reformer operating condition. The assumption here is that the annual investment charges for those equipment items and operating costs not considered for each case remained the same for each case.

Operating costs were based on a 350 day per year operating schedule. General and administrative charges and allocation charges, at the rate of 13% of operating costs, were added to these operating costs. Reformer fuel costs were based on the radiant duty requirement of the reformer. Power costs were calculated from the BHP requirement of the four compressors and small equipment used in the carbon dioxide removal system.

Equipment costs were determined by scaling LaPorte II costs by the ratio of the equipment size to an appropriate power. The LaPorte II reformer had a radiant duty requirement of 62.37 million BTU/hr. From economic data the cost was estimated at approximately $1,581,000

(includes auxiliary equipment plus installation costs). The reformer costs for each case of reformer operating conditions were scaled according to their radiant duty requirement. The multiservice compressor for LaPorte II was rated as 2045 BHP and cost $845,000 (includes motor plus installation costs). The compressor costs for each case were scaled by their total BHP requirement. The carbon dioxide removal system for LaPorte II was capable of removing 220.6 pound moles per hour of carbon dioxide from the reformer and low temperature shift converter effluent streams. This unit cost approximately $808,000 (includes auxiliary equipment and installation costs). The carbon dioxide removal system costs for each case studied were scaled by the total amount of carbon dioxide which had to be removed from the reformer and low temperature shift converter effluent streams.

A cold box analysis was made using the reformer conditions of 1750 ^{o}F, 125 psia and .0048 methane leakage fraction. The purpose of this analysis was to see what affect the methane leakage of the cold box feed stream had on refrigeration requirements. Since methane, when letdown in pressure, supplies more refrigeration per pound mole than other components in the cold box feed stream it was felt that the lower the methane leakage the greater the refrigeration requirement on the nitrogen refrigeration system. The cold box analysis confirmed this. For this methane leakage case of .0048 the total high pressure nitrogen flow to the cold box was 1073 pound moles per hour. For the LaPorte II case (methane leakage of .02) the total high pressure nitrogen flow

to the cold box was 1048.8 pound moles per hour. The differences in methane leakage for each of the 42 cases studied resulted in changes in cold box nitrogen refrigeration requirements, nitrogen compressor BHP requirements and finally the cost of the nitrogen compressors. Using the LaPorte II cold box information and that for the 1750 ^{o}F, 125 psia and .0048 methane leakage case a linear equation was developed which relates the methane leakage for any case to the BHP requirement of the nitrogen compressor for that case. This equation is as follows:

N_2 Compressor BHP = (1594.4 - 2420.5 x CH_4 Leakage Fraction)

(Although this equation is a rough approximation to the actual N_2 compressor BHP for any case it was considered sufficient for its intended purpose. The time needed to develop a more exact equation was not justified since the N_2 compressor costs, calculated for each case through the use of this equation, were not significantly different).

The cost of the nitrogen compressor was calculated for each case. These compressor costs were scaled from the LaPorte II nitrogen compressor which was rated at 1547 BHP and cost $675,000 installed. Since the nitrogen compressor is steam driven no correction had to be made to the power cost of each case.

If the size of a piece of equipment for any particular case was larger than the size of the corresponding LaPorte II equipment the cost was scaled to the .8 power. If the size was smaller than

the LaPorte II equipment size the cost was scaled to the .6 power. For example, assume that a reformer for one case had a radiant duty requirement of 61.00 million BTU/hr. and a reformer for a second case had a radiant duty requirement of 64.00 million BTU/hr. The cost of these two reformers would be calculated as follows:

$$\text{Cost for Reformer \#1} = \left[\frac{61.00 \text{ MM BTU/hr.}}{62.37 \text{ MM BTU/hr.}}\right]^{.6} \times \$1,581,000$$

$$= \$1,560,000$$

$$\text{Cost for Reformer \#2} = \left[\frac{64.00 \text{ MM BTU/hr.}}{62.37 \text{ MM BTU/hr.}}\right]^{.8} \times \$1,581,000$$

$$= \$1,613,000$$

The calculation section illustrates the procedure for costing all the equipment items for the case of reformer operating conditions of 1750 ^{o}F and 175 psia.

The results of annual investment charge versus reformer operating conditions for the 42 cases are shown on Figure 5 and Tables 7a, 7b and 7c. Considering temperature alone, Figure 5 indicates that the lower the temperature the higher the annual investment charge. The carbon dioxide removal system appears to be the controlling factor. Because the shift reaction in the reformer which produces the carbon dioxide is favored with decreasing temperature the carbon dioxide production tends to increase with decreasing temperature. As a result,

the carbon dioxide removal system cost increases with decreasing temperature. Considering the pressure effect in the low temperature region the compressor costs decrease with increasing pressure. The cold box operates at a pressure of about 300 psia, higher than any reformer pressure. As a result, the higher the reformer pressure the smaller the pressure differential between the reformer and cold box and the smaller the compression requirement of the cold box feed compressor (since the carbon monoxide product compression requirement is constant and the carbon dioxide recycle compression requirement is small the cold box feed compression controls the total BHP requirement of the multiservice compressor). This decreasing compression cost, however, is more than offset by the combined increasing reformer and carbon dioxide removal system costs. The net effect is that at low temperature the annual investment charge increases with increasing pressure. However, as the temperature increases the annual investment charges for the higher pressure cases decreases more rapidly than do those of the lower pressure cases.

Figure 5 shows no minimum annual investment charge for any one case but indicates that reformer temperatures higher then 1800 ^{o}F would be even more economical than any of the 42 cases studied. Rather than investigate higher temperatures, however, another aspect was studied.

A reformer tube cost study was made. As the reformer operating temperature and pressure increase the tube stress also increases. In order to withstand the increasing stress the tube wall thickness must be increased or a stronger alloy must be used. In either case the cost

of tubes increases as the reformer operating conditions become more severe. For each case of reformer operating conditions the tube costs were calculated. These calculations required determining the following conditions:

(1) tube length

(2) number of tubes

(3) tube wall thickness based on 4.0 inch I.D. and 100,000 hours of operation for three types of alloys;

a. HK-40 (25% Cr - 20% Ni)

b. Mo-Re #1 (30% Cr - 35% Ni)

c. Super-Therm (26% Cr - 35% Ni)

(4) selection of the more economical alloy with the criterion that tube wall thicknesses were not allowed to exceed .8 inches for fabrication reasons.

All cases were based on 4.0 inch I.D. tubes since this size represented the more economical selection as indicated by a study of tube I.D. versus cost. Tables 8a, 8b and 8c list the calculated tube costs for each case. At the 1550 ^{o}F - 100 psia case the tube cost was $42,000 for HK-40 tubes. This cost represented about 3% of the total reformer cost for this case. At the 1800 ^{o}F - 150 psia case the tube cost was $235,000 for Super-Therm. This cost represented about 15% of the total reformer cost for this case. When the reformer costs for each case were originally arrived at by scaling procedures the percentage cost for reformer tubes remained constant at about 10% (the LaPorte II reformer tube cost amounted to about 10% of the total reformer cost).

RESULTS

Results of this study have indicated that the more favorable reformer operating conditions, from an economic standpoint, fall in the range of 1650 °F to 1750 °F and 125 psia to 200 psia. Specifically, the 1750 °F - 175 psia case represents the most economical selection for reformer operating conditions. However, the annual investment charge for this case is not much lower than any other case within the range mentioned (see Figure 6 for annual investment charge versus reformer operating conditions). The relative difference between this case and the original LaPorte II case of 1650 °F - 185 psia remains to be considered.

Table 9 compares the LaPorte II case with the 1750 °F - 175 psia case. In this table the LaPorte II case is based on the original reformer design which uses 4.5 inch I.D. tubes. The 1750 °F - 175 psia case (as well as all other cases studied) was based on 4.0 inch I.D. reformer tubes. The differential investment charge for these two cases is $40,300 annually, favoring the 1750 °F - 175 psia case (note that the equipment investment charge accounts for 94.5% of this difference, indicating very little difference in operating costs for these two cases). This simply means that, had the LaPorte II reformer been designed to operate at an outlet temperature of 1750 °F and an outlet pressure of 175 psia instead of 1650 °F and 185 psia the annual investment for this plant could have been reduced by $40,300.

The LaPorte II annual equipment and operating cost of those items included in this study amounted to $1,906,300. The annual saving of $40,300 for the 1750 ^{o}F - 175 psia case represents only a 2.1% decrease in the annual investment charge over the LaPorte II case. While the $40,300 may seem significant in itself, the annual investment charge percentage reduction is quite small. The question remains as to whether this percentage reduction would justify evaluating the accuracy of these results or whether an area other than process operating conditions, such as a variation of the process design, might offer more attractive savings.

APPENDIX I

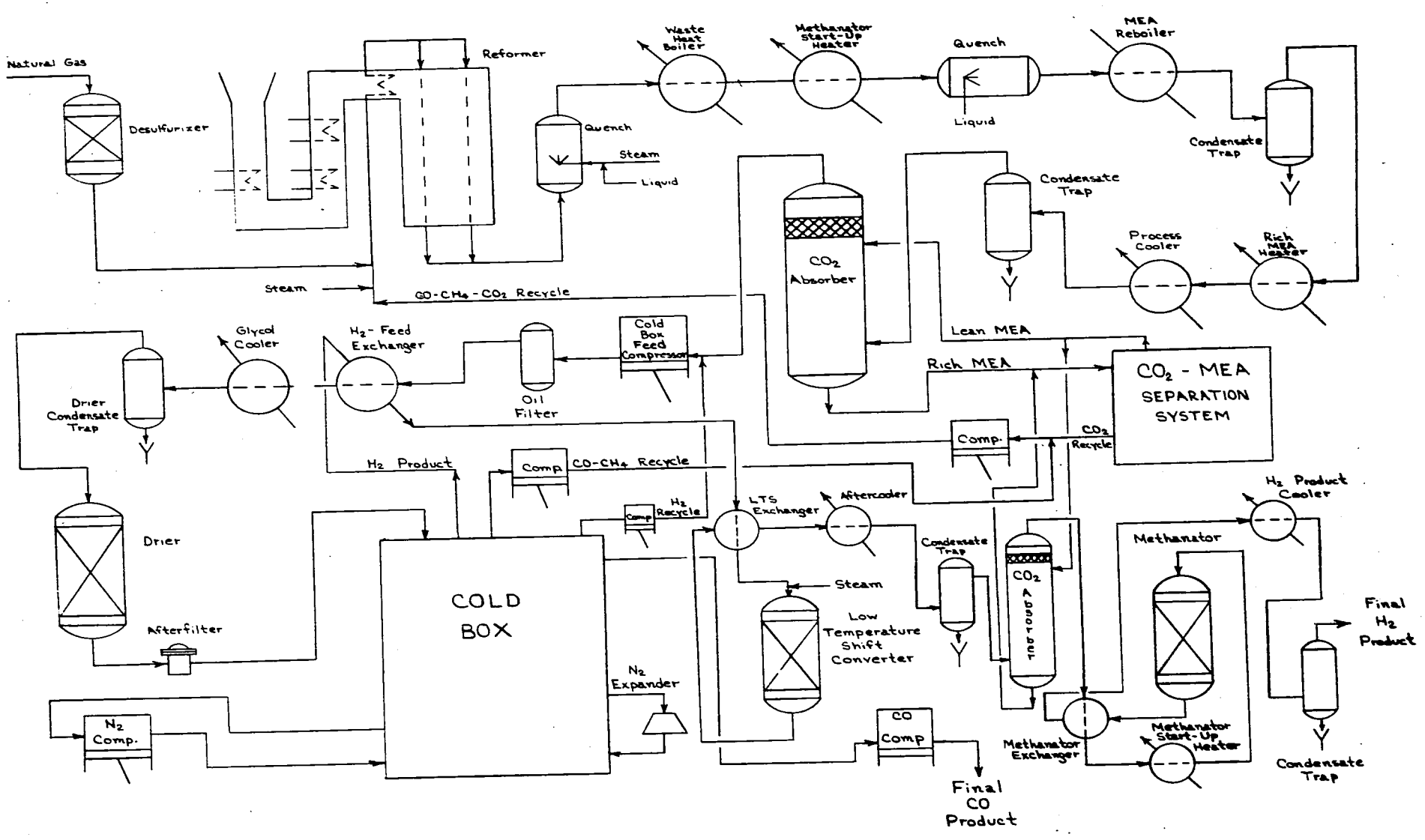

Natural Gas
Desulfurizer
Reformer
Steam
CO-CH4-CO2 Recycle
Waste Heat Boiler
Methanator start-Up Heater
Quench
MEA Reboiler
Liquid
Condensate Trap
Quench
Steam
Liquid
Condensate Trap
CO2 Absorber
Process Cooler
Rich MEA Heater
Lean MEA
Rich MEA
CO2 - MEA SEPARATION SYSTEM
Comp.
CO2 Recycle
Glycol Cooler
H2- Feed Exchanger
Cold Box Feed Compressor
Oil Filter
Drier Condensate Trap
H2 Product
Comp
CO-CH4 Recycle
H2 Recycle
LTS Exchanger
Aftercooler
H2 Product Cooler
Drier
Afterfilter
COLD BOX
Steam
Low Temperature Shift Converter
CO2 Absorber
Methanator
Final H2 Product
N2 Expander
N2 Comp.
CO Comp
Methanator Exchanger
Methanator Start-Up Heater
Condensate Trap
Final CO Product

FIGURE 1

FIGURE 2

Carbon Formation Constant, K_1,
Versus Temperature

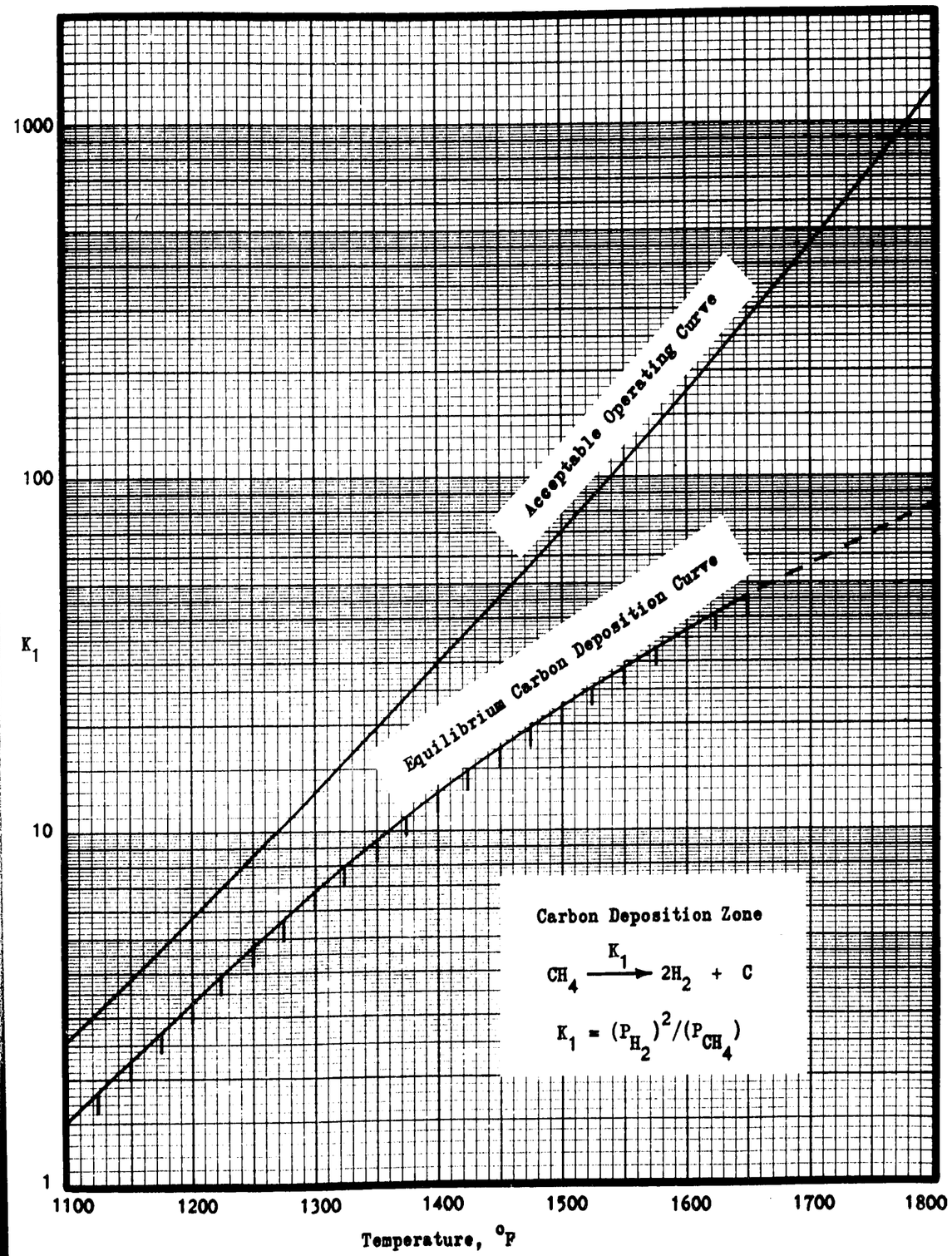


FIGURE 3

Carbon Formation Constant, K_2,
Versus Temperature

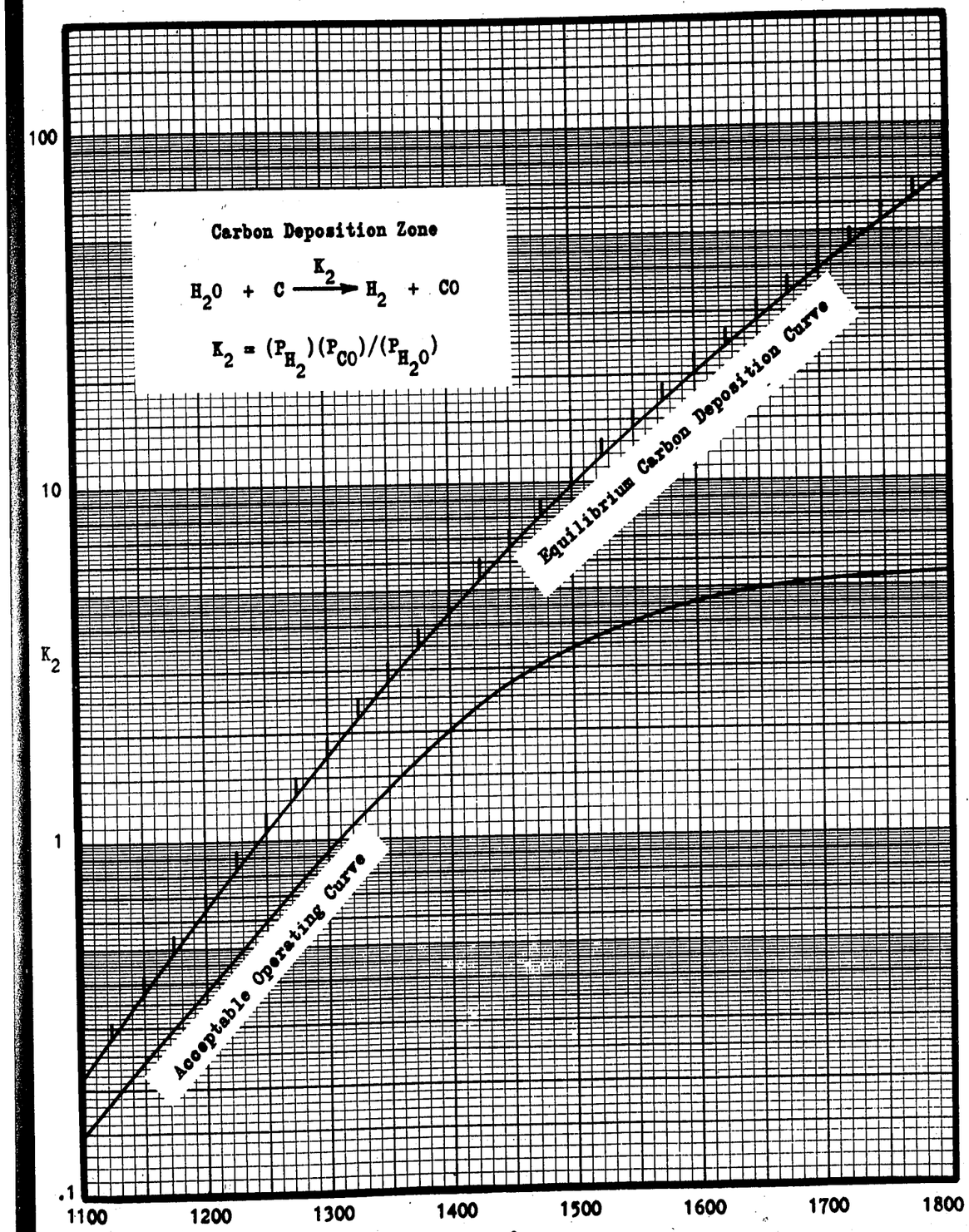


FIGURE 4

Carbon Formation Constant, K_3,
Versus Temperature

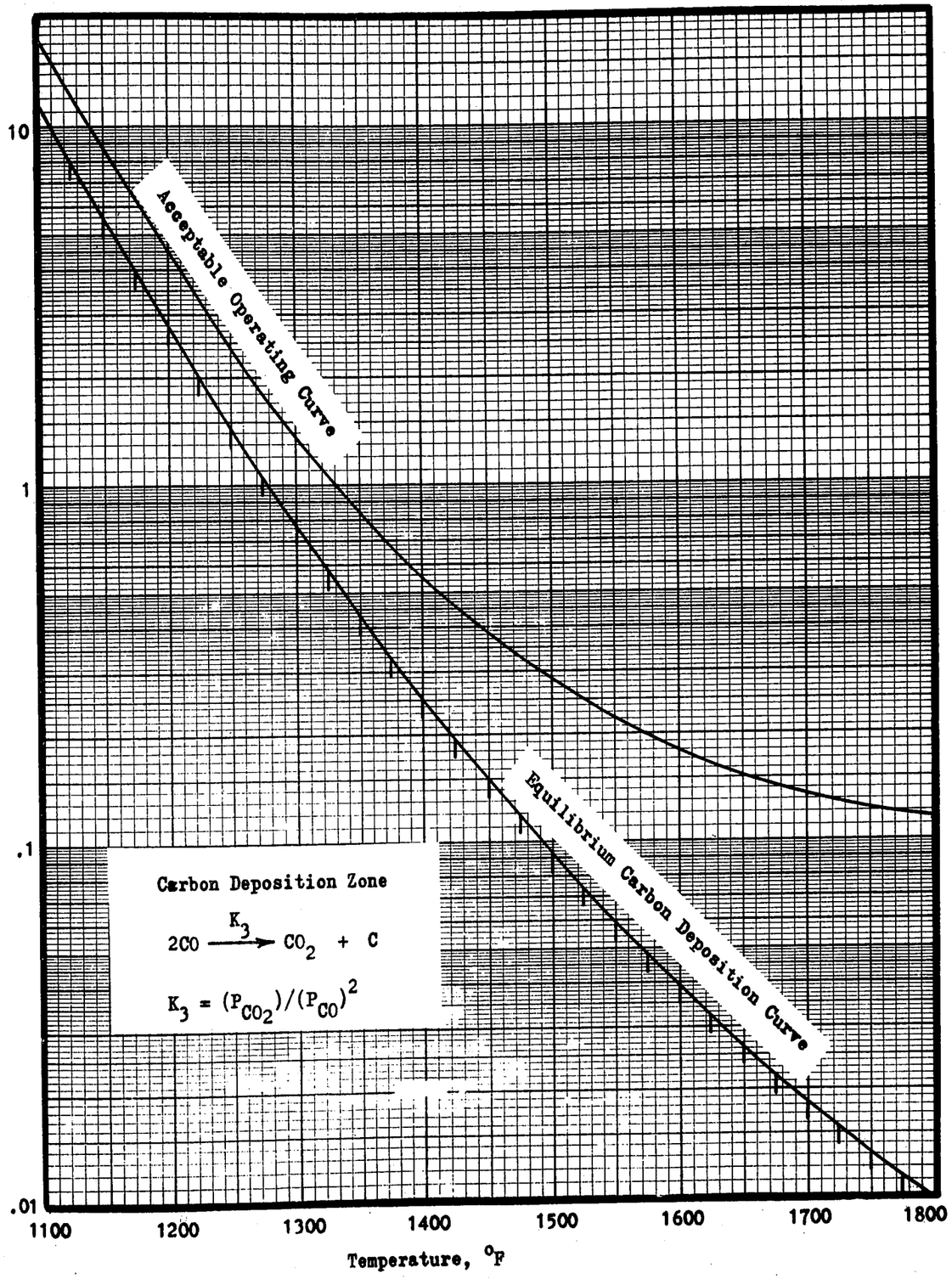


FIGURE 5

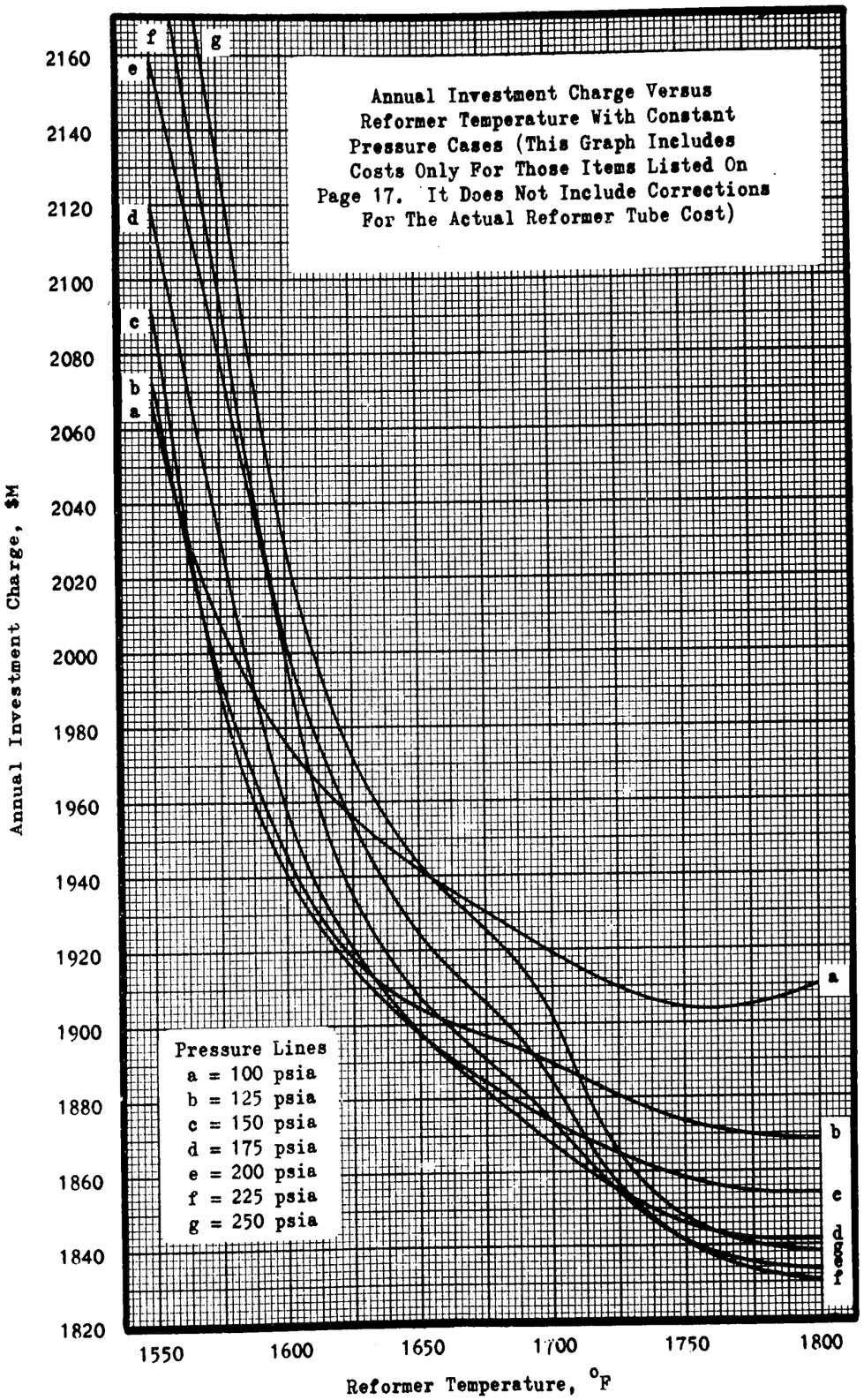

Annual Investment Charge Versus Reformer Temperature With Constant Pressure Cases (This Graph Includes Costs Only For Those Items Listed On Page 17. It Does Not Include Corrections For The Actual Reformer Tube Cost)
Annual Investment Charge, $M
2160
2140
2120
2100
2080
2060
2040
2020
2000
1980
1960
1940
1920
1900
1880
1860
1840
1820
1550
1600
1650
1700
1750
1800
Reformer Temperature, °F
Pressure Lines
a = 100 psia
b = 125 psia
c = 150 psia
d = 175 psia
e = 200 psia
f = 225 psia
g = 250 psia
a
b
c
d e f g

FIGURE 6

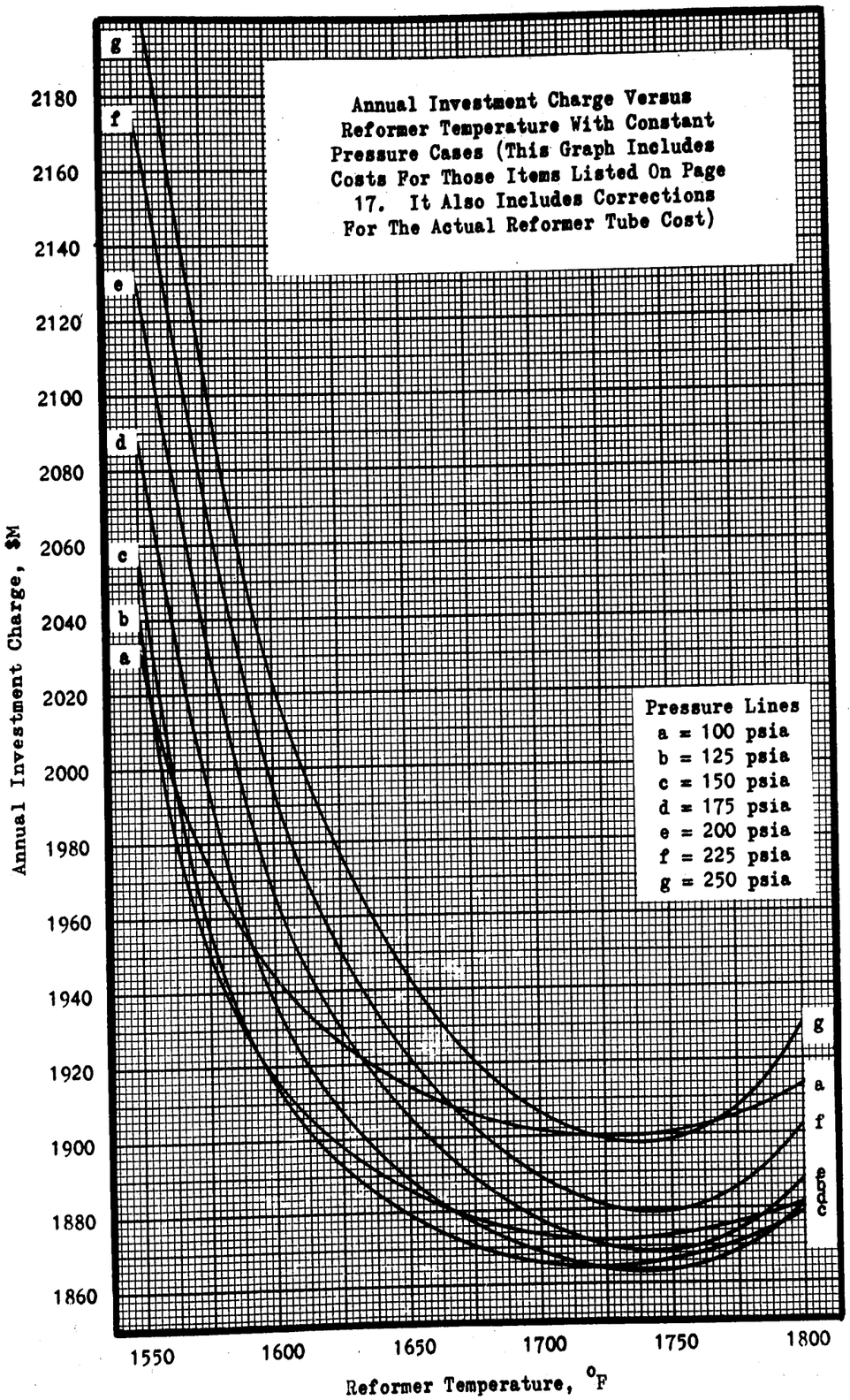

Annual Investment Charge Versus Reformer Temperature With Constant Pressure Cases (This Graph Includes Costs For Those Items Listed On Page 17. It Also Includes Corrections For The Actual Reformer Tube Cost)
Pressure Lines
a = 100 psia
b = 125 psia
c = 150 psia
d = 175 psia
e = 200 psia
f = 225 psia
g = 250 psia
Annual Investment Charge, $M
2180
2160
2140
2120
2100
2080
2060
2040
2020
2000
1980
1960
1940
1920
1900
1880
1860
1550
1600
1650
1700
1750
1800
Reformer Temperature, °F

TABLE 1

Natural Gas Specifications

(LaPorte, Texas)

Component	Percent
CH_4	97.97
C_2H_6	1.37
CO_2	.30
N_2	.36

Hydrogen Product Design Specifications

Component	Percent	Design Rate
H_2	99.73	1382.13
CH_4	.20	2.77
H_2O	.05	.74
N_2	.02	.29

Carbon Monoxide Product Design Specifications

Component	Percent	Design Rate
CO	99.66	459.72
H_2	.002	.01
CH_4	.04	.19
N_2	.30	1.37

TABLE 2

Equilibrium Constants Of The Reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Temp °F	K_s	Temp °F	K_s	Temp °F	K_s	Temp °F	K_s	Temp °F	K_s
400	207	595	32.5	785	9.85	1050	3.13	1430	1.13
405	195	600	31.4	790	9.55	1060	3.03	1440	1.11
410	184	605	30.2	795	9.29	1070	2.93	1450	1.08
415	174	610	29.1	800	9.03	1080	2.83	1460	1.06
420	165	615	28.1	805	8.80	1090	2.74	1470	1.04
425	156	620	27.1	810	8.59	1100	2.65	1480	1.02
430	147	625	26.6	815	8.36	1110	2.57	1490	1.00
435	140	630	25.3	820	8.17	1120	2.49	1500	0.981
440	132	635	24.4	825	7.96	1130	2.41	1510	0.963
445	125	640	23.6	830	7.77	1140	2.34	1520	0.947
450	119	645	22.8	835	7.57	1150	2.27	1530	0.930
455	113	650	22.0	840	7.39	1160	2.20	1540	0.912
460	107	655	21.3	845	7.21	1170	2.14	1550	0.894
465	102	660	20.6	850	7.05	1180	2.08	1560	0.880
470	97.5	665	19.9	855	6.87	1190	2.02	1570	0.864
475	92.4	670	19.3	860	6.71	1200	1.97	1580	0.849
480	88.0	675	18.6	865	6.56	1210	1.92	1590	0.834
485	83.9	680	18.0	870	6.41	1220	1.86	1600	0.819
490	79.9	685	17.5	875	6.28	1230	1.81	1610	0.804
495	76.2	690	16.9	880	6.14	1240	1.76	1620	0.791
500	72.8	695	16.4	885	6.00	1250	1.72	1630	0.779
505	69.5	700	15.9	890	5.87	1260	1.67	1640	0.766
510	66.5	704	15.4	895	5.75	1270	1.63	1650	0.754
515	63.5	710	14.9	900	5.61	1280	1.59	1660	0.741
520	60.8	715	14.5	910	5.39	1290	1.55	1670	0.729
525	58.1	720	14.1	920	5.15	1300	1.51	1680	0.719
530	55.7	725	13.7	930	4.94	1310	1.48	1690	0.708
535	53.2	730	13.3	940	4.73	1320	1.44	1700	0.697
540	51.0	735	12.9	950	4.55	1330	1.41	1710	0.685
545	48.8	740	12.5	960	4.36	1340	1.38	1720	0.675
550	46.7	745	12.2	970	4.19	1350	1.34	1730	0.665
555	44.8	750	11.8	980	4.02	1360	1.31	1740	0.656
560	43.0	755	11.5	990	3.88	1370	1.28	1750	0.647
565	41.4	760	11.2	1000	3.75	1380	1.26	1760	0.638
570	39.8	765	10.9	1010	3.61	1390	1.23	1770	0.629
575	38.1	770	10.6	1020	3.47	1400	1.20	1780	0.620
580	36.6	775	10.3	1030	3.35	1410	1.18	1790	0.612
590	33.8	780	10.1	1040	3.23	1420	1.15	1800	0.604

TABLE 3

Equilibrium Constants Of The Reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Temp °F	K_r	Temp °F	K_r	Temp °F	K_r
900	.004334	1250	6.327	1600	817.8
910	.005608	1260	7.468	1610	917.6
920	.007231	1270	8.799	1620	1028
930	.009291	1280	10.35	1630	1151
940	.01190	1290	12.15	1640	1288
950	.01518	1300	14.23	1650	1438
960	.01931	1310	16.65	1660	1605
970	.02449	1320	19.44	1670	1790
980	.03095	1330	22.66	1680	1993
990	.03900	1340	26.37	1690	2218
1000	.04899	1350	30.64	1700	2466
1010	.06136	1360	35.54	1710	2738
1020	.07662	1370	41.16	1720	3038
1030	.09541	1380	47.60	1730	3367
1040	.1185	1390	54.95	1740	3729
1050	.1467	1400	63.35	1750	4125
1060	.1812	1410	72.92	1760	4560
1070	.2231	1420	83.81	1770	5036
1080	.2741	1430	96.19	1780	5557
1090	.3358	1440	110.2	1790	6126
1100	.4104	1450	126.2	1800	6748
1110	.5004	1460	144.2	1810	7426
1120	.6085	1470	164.6	1820	8167
1130	.7383	1480	187.6	1830	8973
1140	.8937	1490	213.5	1840	9851
1150	1.079	1500	242.7	1850	10810
1160	1.300	1510	275.6	1860	11850
1170	1.563	1520	312.5	1870	12970
1180	1.876	1530	353.9	1880	14200
1190	2.245	1540	400.3	1890	15530
1200	2.682	1550	452.2	1900	16970
1210	3.197	1560	510.3	1910	18530
1220	3.803	1570	575.2	1920	20220
1230	4.515	1580	647.5	1930	22040
1240	5.350	1590	728.1	1940	24020

TABLE 4

Approach To Equilibrium Criterion *

Reformer Outlet Temp. °F	ATE °F	Equilibrium Temp. For K_r °F	K_r	Equilibrium Temp. For K_s °F	K_s
1550	50	1500	242.7	1550	0.894
1600	30	1570	575.2	1600	0.819
1650	30	1620	1028	1650	0.754
1700	30	1670	1970	1700	0.697
1750	20	1730	3367	1750	0.647
1800	20	1780	5557	1800	0.604

Theoretical Equilibrium Criterion **

Reformer Outlet Temp. °F	ATE °F	Equilibrium Temp. For K_r °F	K_r	Equilibrium Temp. For K_s °F	K_s
1550	0	1550	452.2	1550	0.894
1600	0	1600	817.8	1600	0.819
1650	0	1650	1438	1650	0.754
1700	0	1700	2466	1700	0.697
1750	0	1750	4125	1750	0.647
1800	0	1800	6748	1800	0.604

* Used in calculating the expected or actual reformer effluent and feed compositions.

** Used in calculating intermediate and outlet reformer conditions to determine carbon formation constants and to check the methane leakage.

TABLE 5

Computer Output For Reformer Calculations

Actual Operating Conditions

For Sample Calculations

Specie	Inlet Moles *	Outlet Moles *
CH_4	466.454	14.310
CO_2	158.955	134.631
CO	14.100	503.220
H_2	0.000	1363.740
N_2	1.662	1.662
C_2H_6	6.325	0.000
Dry Total	647.496	2017.563
H_2O	1003.959	563.485
Wet Total	1651.455	2581.048
Temperature, ^oF	900	1750
Pressure, psia		175

Steam To Carbon Ratio = 1.5394

Radiant Duty = 62.564 MM BTU/hr

Approach To Equilibrium = 20 ^oF

Methane Leakage Fraction = 0.0076

* Flow rates are in pound moles per hour.

TABLE 6a

Computer Output For Reformer Calculations

Theoretical Operating Conditions

For Sample Calculations

Specie	Inlet Moles *	Outlet Moles *
CH_4	466.454	368.240
CO_2	158.955	238.886
CO	14.100	44.998
H_2	0.000	406.073
N_2	1.662	1.662
C_2H_6	6.325	0.000
Dry Total	647.496	1059.857
H_2O	1003.959	813.227
Wet Total	1651.455	1873.084
Temperature, ^oF	900	1100
Pressure, psia		175

Approach To Equilibrium = 0 ^oF

Carbon Formation Constants

K_1 = 2.8466

K_2 = 0.14284

K_3 = 18.558

* Flow rates are in pound moles per hour.

TABLE 6b

Computer Output For Reformer Calculations

Theoretical Operating Conditions

For Sample Calculations

Specie	Inlet Moles *	Outlet Moles *
CH_4	466.454	132.074
CO_2	158.955	199.239
CO	14.100	320.714
H_2	0.000	1074.630
N_2	1.662	1.662
C_2H_6	6.325	0.000
Dry Total	647.496	1728.391
H_2O	1003.959	616.808
Wet Total	1651.455	2345.127
Temperature, ^oF	900	1450
Pressure, psia		175

Approach To Equilibrium = 0 ^oF

Carbon Formation Constants

K_1 = 44.391

K_2 = 2.8367

K_3 = 0.38154

* Flow rates are in pound moles per hour

TABLE 6c

Computer Output For Reformer Calculations

Theoretical Operating Conditions

For Sample Calculations

Specie	Inlet Moles *	Outlet Moles *
CH_4	466.454	11.941
CO_2	158.955	134.246
CO	14.100	505.947
H_2	0.000	1370.360
N_2	1.662	1.662
C_2H_6	6.325	0.000
Dry Total	647.496	2024.156
H_2O	1003.959	561.559
Wet Total	1651.455	2585.715
Temperature, ^oF	900	1750
Pressure, psia		175

Approach To Equilibrium = 0 ^oF

Carbon Formation Constants

K_1 = 724.20

K_2 = 5.6857

K_3 = 0.11388

* Flow rates are in pound moles per hour.

TABLE 7a

Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Operating Cost [1]	Compressor Cost [2]	Reformer Cost	CO_2 Removal System Cost	Sealed Tube Cost	Annual Investment Charge [3]
Temp ^oF	Press psia	CH_4 Leakage Fraction	$M/yr	$M	$M	$M	$M	$M/yr
1650	185	.020	644	1519	1581	808	155	1906
1550	100	.028	682	1879	1541	868	151	2068
1550	125	.034	677	1777	1559	984	153	2072
1550	150	.040	677	1714	1575	1088	155	2091
1550	175	.046	681	1674	1593	1185	156	2119
1550	200	.050	687	1649	1615	1292	159	2158
1550	225	.054	695	1634	1635	1393	161	2201
1550	250	.058	704	1629	1654	1488	162	2244
1600	100	.018	665	1827	1531	697	150	1975
1600	125	.024	653	1714	1542	742	151	1945
1600	150	.028	649	1637	1556	803	153	1940
1600	175	.030	650	1583	1571	895	154	1958
1600	200	.032	653	1544	1587	983	156	1982

1 Includes reformer fuel and electrical power costs.
2 Includes multiservice plus nitrogen compressor costs.
3 Includes only those items considered in this table (not including corrections for reformer tube costs).

TABLE 7b

Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Operating Cost [1]	Compressor Cost [2]	Reformer Cost	CO_2 Removal System Cost	Sealed Tube Cost	Annual Investment Charge [3]
Temp °F	Press psia	CH_4 Leakage Fraction	$M/yr	$M	$M	$M	$M	$M/yr
1600	225	.036	656	1517	1601	1043	157	2000
1600	250	.038	661	1499	1618	1119	159	2030
1650	100	.012	661	1803	1535	625	151	1941
1650	125	.016	647	1682	1545	664	152	1904
1650	150	.018	643	1598	1559	725	153	1897
1650	175	.020	641	1538	1572	778	154	1897
1650	200	.022	642	1498	1585	833	156	1907
1650	225	.024	644	1472	1600	892	157	1924
1650	250	.026	646	1451	1614	948	159	1943
1700	100	.0080	660	1786	1541	570	151	1919
1700	125	.0096	648	1662	1554	625	153	1889
1700	150	.0112	642	1574	1567	673	154	1873
1700	175	.0128	638	1512	1578	715	155	1868
1700	200	.0140	638	1475	1593	760	156	1874
1700	225	.0152	639	1444	1608	801	158	1884

1.2.3 See Table 7a for notation.

TABLE 7c

Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Operating Cost [1]	Compressor Cost [2]	Reformer Cost	CO_2 Removal System Cost	Scaled Tube Cost	Annual Investment Charge [3]
Temp ^oF	Press psia	CH_4 Leakage Fraction	$M/yr	$M	$M	$M	$M	$M/yr
1700	250	.0160	642	1421	1624	856	159	1902
1750	100	.0048	661	1774	1548	526	152	1904
1750	125	.0056	649	1647	1562	582	153	1874
1750	150	.0064	642	1557	1575	630	155	1858
1750	175	.0076	637	1497	1585	660	156	1846
1750	200	.0088	634	1455	1596	688	157	1841
1750	225	.0100	632	1420	1606	714	158	1840
1750	250	.0108	633	1392	1620	747	159	1847
1800	100	.0028	668	1768	1563	515	153	1910
1800	125	.0036	653	1638	1573	551	154	1868
1800	150	.0040	647	1547	1589	601	156	1854
1800	175	.0048	641	1488	1600	627	157	1841
1800	200	.0056	637	1444	1611	652	158	1834
1800	225	.0064	634	1407	1620	675	159	1830
1800	250	.0068	636	1378	1635	709	161	1838

1,2,3 See Table 7a for notation

TABLE 8a

Revised Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Scaled Tube Cost $M	Actual Tube Cost [1] $M	Tube Material	Adjusted Annual Investment Charge $M/yr
Temp °F	Press psia	CH_4 Leakage Fraction				
1550	100	.028	151	42	HK-40	2032
1550	125	.034	153	49	HK-40	2039
1550	150	.040	155	57	HK-40	2059
1550	175	.046	156	64	HK-40	2089
1550	200	.050	159	73	HK-40	2131
1550	225	.054	161	83	HK-40	2176
1550	250	.058	162	93	HK-40	2222
1600	100	.018	150	51	HK-40	1943
1600	125	.024	151	60	HK-40	1915
1600	150	.028	153	71	HK-40	1913
1600	175	.030	154	82	HK-40	1935
1600	200	.032	156	94	HK-40	1962

1 This tube cost applies to 4.0 inch I.D. tubes for all cases of reformer operating conditions.

TABLE 8b

Revised Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Scaled Tube Cost $M	Actual Tube Cost [1] $M	Tube Material	Adjusted Annual Investment Charge $M/yr
Temp °F	Press psia	CH_4 Leakage Fraction				
1600	225	.036	157	123	S - Therm	1984
1600	250	.038	159	139	S - Therm	2019
1650	100	.012	151	66	HK-40	1914
1650	125	.016	152	79	HK-40	1880
1650	150	.018	153	94	HK-40	1878
1650	175	.020	154	123	S - Therm	1887
1650	200	.022	156	138	S - Therm	1901
1650	225	.024	157	155	S - Therm	1923
1650	250	.026	159	173	S - Therm	1947
1700	100	.0080	151	87	HK-40	1908
1700	125	.0096	153	117	S - Therm	1878
1700	150	.0112	154	136	S - Therm	1868
1700	175	.0128	155	156	S - Therm	1868
1700	200	.0140	156	178	S - Therm	1881
1700	225	.0152	158	202	S - Therm	1898

1 See Table 8a for notation.

TABLE 8c

Revised Economic Data For
Reformer Operating Conditions

Reformer Operating Conditions			Scaled Tube Cost	Actual Tube Cost [1]	Tube Material	Adjusted Annual Investment Charge
Temp °F	Press psia	CH_4 Leakage Fraction	$M	$M		$M/yr
1700	250	.0160	159	228 *	S - Therm	1924
1750	100	.0048	152	125	S - Therm	1895
1750	125	.0056	153	149	S - Therm	1872
1750	150	.0064	155	175	S - Therm	1864
1750	175	.0076	156	204	S - Therm	1861
1750	200	.0088	157	236 *	S - Therm	1867
1750	225	.0100	158	271 *	S - Therm	1877
1750	250	.0108	159	311 *	S - Therm	1896
1800	100	.0028	153	161	S - Therm	1913
1800	125	.0036	154	195	S - Therm	1881
1800	150	.0040	156	235	S - Therm	1880
1800	175	.0048	157	279 *	S - Therm	1880
1800	200	.0056	158	329 *	S - Therm	1889
1800	225	.0064	159	387 *	S - Therm	1904
1800	250	.0068	161	457 *	S - Therm	1934

1 See Table 8a for notation
* Indicates that the tube wall thickness is greater than maximum allowable thickness of .8 inches.

TABLE 9

Economic Comparative Data For The
Original LaPorte II Case And
The Case Of 1750 ^{o}F and 175 psia

Cost Item	LaPorte II Case	1750 ^{o}F - 175 psia Case
Compressors [1]	$1,519,400	$1,496,900
CO_2 Removal System	808,000	660,300
Reformer [2]	1,581,000	1,633,200
Equipment Cost	$3,908,400	$3,790,400
Annual Equipment Investment Charge	$1,262,400	$1,224,300
Annual Operating [3] Cost	643,900	636,900
Steam System Cost Differential	0	4,800
Adjusted Annual Operating Cost	643,900	641,700
Annual Investment [4] Charge	$1,906,300	$1,866,000

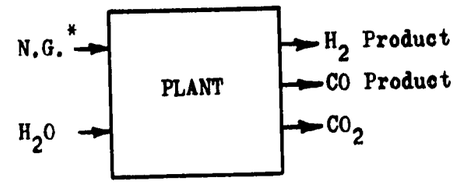
1 Includes multiservice compressor and nitrogen refrigeration compressor.
2 Includes actual reformer tube cost (not scaled tube cost).
3 Includes reformer fuel and electrical power cost.
4 Includes annual equipment investment charge and annual operating cost (including steam system cost differential) only for those items considered. This is not the total plant annual investment charge.

APPENDIX II

SAMPLE CALCULATIONS

This section illustrates the technique of calculating reformer flow rates from known hydrogen and carbon monoxide product rates. All flow rates are in pound moles per hour unless otherwise indicated.

1. First a total plant material balance is made to determine the process natural gas consumption, the amount of carbon dioxide vented from the plant and the amount of water consumed by reaction in the plant (see Table 1 for H_2, CO and natural gas specifications).



Carbon Atom Balance:

$$1.0101\ (N.G.) = CO_2 + 2.77 + 459.72 + 0.19$$

Hydrogen Atom Balance:

$$4.001\ (N.G.) + 2\ (H_2O) = 2\ (1382.13) + 4\ (2.77) + 2\ (.01) + 4\ (.19)$$

Oxygen Atom Balance:

$$.006\ (N.G.) + H_2O = 459.72 + 2\ (CO_2)$$

* Natural Gas

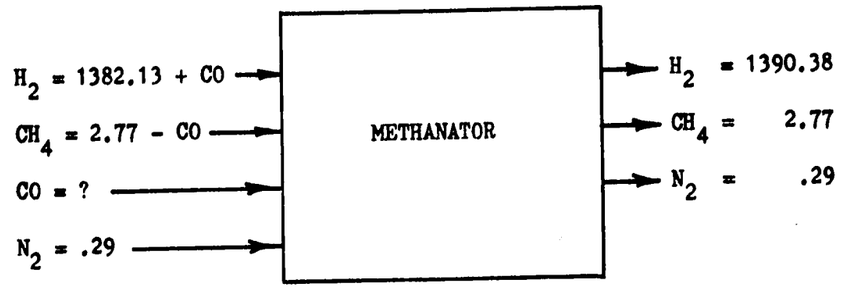
Simultaneous solution of the previous three balance equations yields the following values:

$$N.G. = 461.728$$

$$H_2O = 464.378$$

$$CO_2 = 3.712$$

2. The hydrogen product feed composition to the methanator is now calculated.



$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

It is assumed that the fraction of CH_4 in the hydrogen feed stream to the methanator is .000013. It is further assumed that all the CO_2 in the LTS effluent has been removed in the MEA absorber (this means that there is no CO_2 present in the methanator feed stream).

$\underline{CH_4}$ Balance (on the feed stream to the methanator):

$$.000013\ (1382.13 + CO + 2.77 - CO + CO + .29) = 2.77 - CO$$

$$CO = 2.752$$

Thus the methanator feed stream has the following composition:

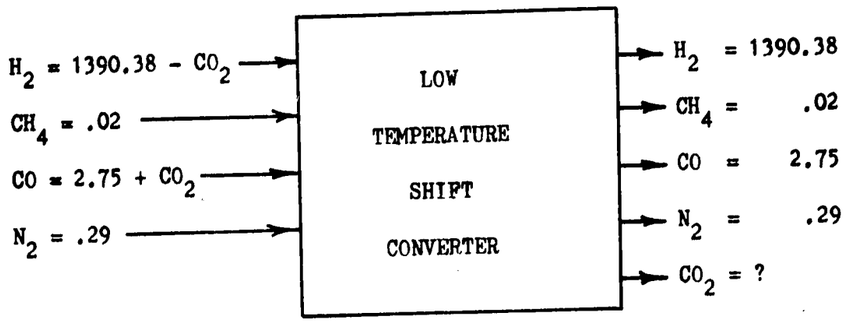
H_2 = 1390.38

CH_4 = .02

CO = 2.75

N_2 = .29

3. The hydrogen product feed composition to the low temperature shift converter is now calculated.



$$CO + H_2O \longrightarrow CO_2 + H_2$$

It is assumed that the fraction of CO present in the hydrogen feed stream is .0211.

<u>CO Balance</u> (on feed stream to the LTS):

$$.0211\ (1390.38 - CO_2 + 2.75 + CO_2 + .02 + .29) = 2.75 + CO_2$$

$$CO_2 = 26.65$$

Thus the LTS feed stream has the following composition:

H_2 = 1363.74
CO = 29.40
CH_4 = .02
N_2 = .29
Total = 1393.44

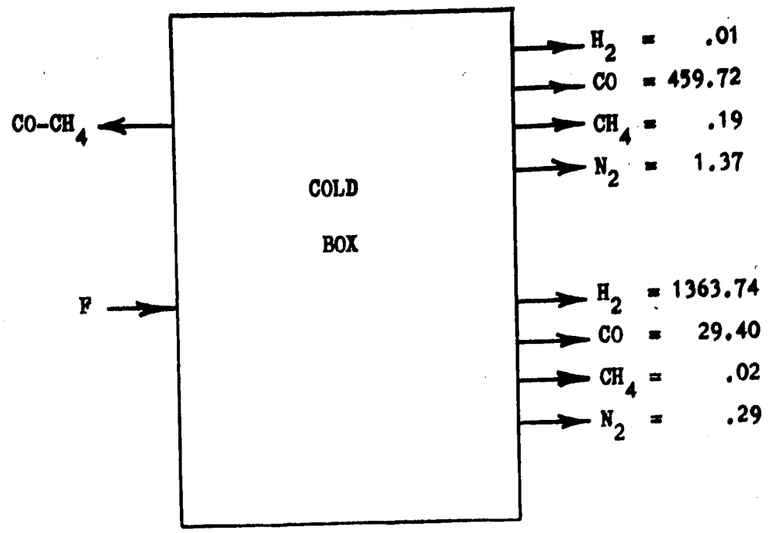
This LTS feed stream also represents the hydrogen product stream leaving the cold box. Since cold box operating conditions remain constant for each case of reformer operating conditions, this hydrogen product stream leaving the cold box is assumed constant for all cases. The final carbon monoxide product composition shown in Table 1 represents the cold box carbon monoxide product stream. This stream is also unaffected by reformer operating conditions.

4. The cold box stream compositions are now calculated.

Let F = total feed to cold box

$CO\text{-}CH_4$ = $CO\text{-}CH_4$ recycle stream from the cold box (50-50 mixture)

Y_{CH_4} = methane leakage from reformer



Total Material Balance

$$F = (CO\text{-}CH_4) + 461.29 + 1393.44 = (CO\text{-}CH_4) + 1854.73$$

CH_4 Balance

$$Y_{CH_4} \times F = .5\ (CO\text{-}CH_4) + .19 + .02$$

$$F = \frac{927.365}{(.5 - Y_{CH_4})}$$

At this point reformer operating conditions must be selected. For purposes of illustration let the reformer have the following operating conditions:

Reformer Outlet Temperature = 1750 ^{o}F

Reformer Outlet Pressure = 175 psia

Reformer Methane Leakage = .0076 fraction = Y_{CH_4}

With the methane leakage set the cold box conditions can now be calculated.

$$P = \frac{927.365}{(.5-.0076)} = 1882.93$$

$$CO\text{-}CH_4 = \frac{1882.93\ (.0076) - .19 - .02}{.5} = 28.202$$

Feed stream compositions to the cold box are as follows:

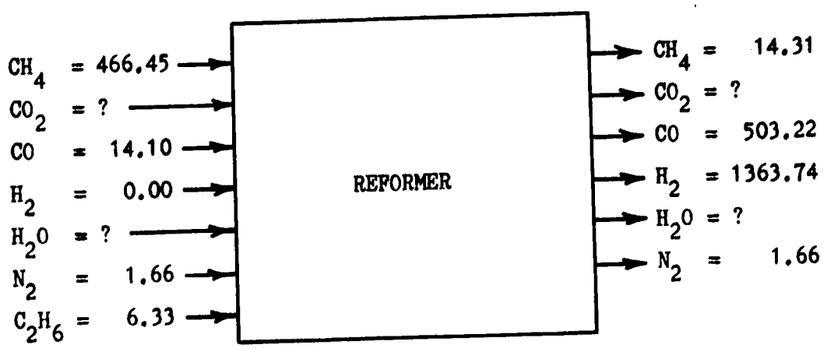
H_2 = 1363.74

CO = 503.22

CH_4 = 14.31

N_2 = 1.66

5. The reformer feed and effluent streams are now calculated.



(1) $CH_4 + H_2O \xrightarrow{K_r} CO + 3H_2$

(2) $CO + H_2O \xrightarrow{K_s} CO_2 + H_2$

The indicated feed streams are calculated from the known quantity of natural gas fed to the plant and the composition of this natural gas feed (see Table 1).

It is assumed that the reforming reaction has a 20 °F approach to equilibrium and the water-gas shift reaction has a 0 °F approach to equilibrium (see Table 4) for the purpose of calculating the actual reformer effluent CO_2 and H_2O compositions. Thus, $K_r = 336.7$ @ 1730 °F and $K_s = 0.647$ @ 1750 °F.

$$(3) \quad K_r = 336.7 = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})} = \frac{(CO)(H_2)^3}{(CH_4)(H_2O)} \times \frac{P^{2\,*}_{outlet}}{(Total\ Moles)^2}$$

$$(4) \quad K_s = 0.647 = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

Equations (3) and (4) are solved simultaneously to yield the effluent CO_2 and H_2O compositions. For this illustration these compositions are as follows:

$CO_2 = 134.63$

$H_2O = 563.48$

* Outlet pressure in atmospheres.

The feed CO_2 and H_2O are now calculated as follows:

Carbon Atom Balance

$$CO_2 + 466.45 + 14.10 + 2\ (6.33) = 14.31 + 134.63 + 503.22$$

$$CO_2 = 158.96$$

Hydrogen Atom Balance

$$4\ (466.45) + 2\ (H_2O) + 3\ (6.33) = 4\ (14.31) + 2\ (1363.74) + 2\ (563.48)$$

$$H_2O = 1003.96$$

A computer program was developed which calculates the cold box and reformer balances. Table 5 is the output for this illustration.

At this point all reformer streams are known. Now the carbon formation criterion must be checked. Using the actual feed conditions theoretical intermediate and an outlet condition are calculated assuming a zero approach to equilibrium for both reforming reactions. Table 6a, 6b and 6c show the output of a computer program used for calculating these theoretical conditions for this illustration. In these tables are shown the carbon formation constants K_1, K_2 and K_3 at the temperatures of 1100 ^oF, 1450 ^oF and 1750 ^oF. These K values are compared to the acceptable operating curves of Figures 2, 3 and 4. If the K values fall within a small range of the curves, the initial value of methane leakage is acceptable. If the K values fall away from the curves, the methane leakage must be adjusted. The cold box and reformer calculations must then be repeated until the carbon formation criterion is

satisfied. The K values calculated for this illustration do fall within a small range of the acceptable operating curves. Therefore, the selected value for the methane leakage, .0076, is acceptable.

6. The equipment and operating costs are now calculated for this illustration using the LaPorte II design and economic data.

   a. The following equation is used to calculate the BHP for the CO_2 recycle compressor, the CO product compressor, the CO-CH_4 recycle compressor and the cold box feed compressor:

$$BHP = \frac{144 \times N \times K \times P_s \times MW \times W}{33{,}000 \times (K-1) \times E \times 60 \times D} \left[\left(\frac{P_d}{P_s} \right)^{\frac{K-1}{K \times N}} - 1 \right]$$

   where: N = number of stages
   K = heat capacity ratio
   P_s = suction pressure, psia
   P_d = discharge pressure, psia
   E = efficiency, fraction
   MW = molecular weight, lb/lb mole
   W = flow rate, lb moles/hr
   D = suction gas density, lb/ft^3

For this illustration the compressors had the following BHP requirements:

Cold Box Feed Compressor BHP = 880.7

CO_2 Recycle Compressor = 256.0

CO-CH_4 Recycle Compressor = 47.4

CO Product Compressor = 740 (constant for all cases)

$$\text{Compressor Cost} = \left(\frac{880.7 + 256.0 + 47.4 + 740}{2045_L} \right)^{.6} \times \$842{,}000_L$$

$$= \$812{,}000$$

b. The nitrogen compressor BHP and cost are determined as follows:

N_2 Compressor BHP = 1594.4 - 2420.47 (.0076) = 1576.0

$$N_2 \text{ Compressor Cost} = \left(\frac{1576}{1547_L} \right)^{.8} \times \$675{,}000_L = \$685{,}000$$

c. The reformer cost (scaled by the radiant duty requirement) is calculated as follows:

$$\text{Reformer Cost} = \left(\frac{62.56 \text{ MM BTU/hr}}{62.37 \text{ MM BTU/hr}_L} \right)^{.8} \times \$1{,}581{,}000_L$$

$$= \$1{,}584{,}800$$

d. The CO_2 removal system cost (scaled by the amount of CO_2 removed from the reformer effluent and LTS effluent) is calculated as follows:

$$CO_2 \text{ Removal System Cost} = \left(\frac{157.56}{220.58_L} \right)^{.6} \times \$808{,}000_L = \$660{,}300$$

L Represents the LaPorte II scaling parameter or cost figure for the specified piece of equipment.

e. The reformer fuel cost is calculated as follows:

$$\text{Fuel Cost} = \frac{62.56 \text{ MM BTU/hr}}{.43 \text{ efficiency}} \times 35¢/\text{MM BTU} \times 1.1059 \text{ HHV/LHV}$$

$$\times 24 \text{ hr/day} \times 350 \text{ day/yr} \times 1.027 \text{ (Allocations)}$$

$$\times 1.099 \text{ (G\&A)} = \$532{,}000/\text{yr}$$

f. The BHP requirement of the small equipment in the CO_2 removal system must be known before the electrical power cost can be determined. This BHP is calculated by scaling from the amount of CO_2 which is removed from the reformer effluent and LTS effluent streams.

$$CO_2 \text{ Removal System BHP} = \left(\frac{155.57}{220.58_L}\right) \times 130 \text{ (BHP for LaPorte II } CO_2 \text{ removal system)}$$

$$= 93$$

g. The electrical power cost is determined from the total BHP requirement of the multiservice compressor and the small equipment in the CO_2 removal system.

$$\text{Power Cost} = (880.7 \text{ BHP} + 256.0 \text{ BHP} + 47.4 \text{ BHP} + 740 \text{ BHP} + 93 \text{ BHP}) \times \$ .007/\text{KWH} \times .7457 \text{ KWH/BHP} \times 1/.96 \text{ efficiency} \times 24 \text{ hr/day} \times 350 \text{ day/yr} \times 1.027 \text{ (Allocations)} \times 1.099 \text{ (G\&A)} = \$105{,}000/\text{yr}$$

h. The equipment cost of the multiservice compressor, nitrogen refrigeration compressor, reformer and carbon dioxide removal system is calculated as $3,742,100. This figure is converted to an annual equipment investment charge by multiplying by the factor .323. This factor includes allowances for maintenance, depreciation, allocations, G&A, gross profits and interest on an annual basis. This annual equipment investment charge is $1,209,000.

i. The annual investment charge for the equipment and operating costs considered is $1,846,000

j. The scaled tube cost is calculated as follows:

$$\text{Scaled Reformer Tube Cost} = \left(\frac{\$155,270}{\$1,581,000}\right) \times \$1,584,800$$

$$= \$155,600$$

The actual tube cost for this case is $204,000. The actual cost of the reformer for this case should then be:

$$\text{Actual Reformer Cost} = \$1,584,800 + (\$204,000 - \$155,600)$$

$$= \$1,633,200$$

The adjucted annual investment charge then becomes $1,861,200 instead of $1,846,000 after the actual reformer tube cost is considered.

SOURCES OF INFORMATION

(1) Blaw Knox Company, National Alloy Division, Pittsburgh, Pennsylvania : supplied information for reformer tube design.

(2) Selas Corporation of America, Dresher, Pennsylvania : supplied information for reformer tube design.

(3) Chemetron Corporation, Louisville, Kentucky : supplied information for reformer and reformer tube design.

(4) Air Products and Chemicals Inc., Allentown, Pennsylvania : supplied all information on LaPorte II design including economic data.